

News Item

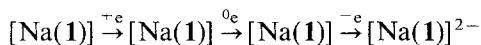
A New Challenge to Valency

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A fundamental tenet of chemistry is that isolatable compounds should be electrically neutral overall – it is not possible to keep a bottle of sodium ions on the shelf. Over the past few years a number of compounds have been described that apparently conflict with this view, and these have provided a challenge to theoreticians and synthetic chemists alike. Lehn and his co-workers have now described another example of such a compound, which has been described as a ‘molecular element’ [1].

Lehn and colleagues are interested in the properties of metal ions ‘imprisoned’ within cage-like molecules [2] such as the cryptand, compound **1** in Figure 1. The reaction of **1** with sodium bromide yields the complex $[\text{Na}(\mathbf{1})]\text{Br}$ in which the sodium cation is trapped within the cage and is bonded to the six nitrogen atoms of the 2,2′-bipyridine subunits. The passage of an electric current through solutions of $[\text{Na}(\mathbf{1})]\text{Br}$ results in current flow at three different potentials corresponding to the formal processes:



The compound $[\text{Na}(\mathbf{1})]$ is formed at the electrode as blue-violet crystals, which are immediately destroyed upon exposure to the air. The crystal structure of this compound has been determined and it shows only an $[\text{Na}(\mathbf{1})]$ unit (Figure 2) – no anions appear to be present.

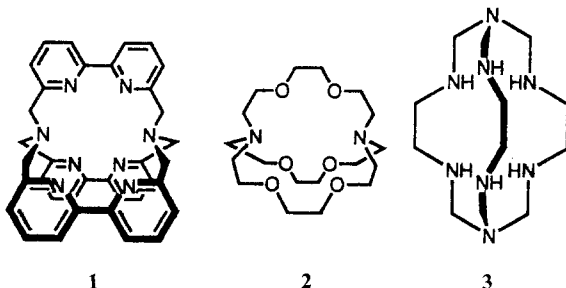


Fig. 1. Three macrocyclic ‘cryptand’ ligands.

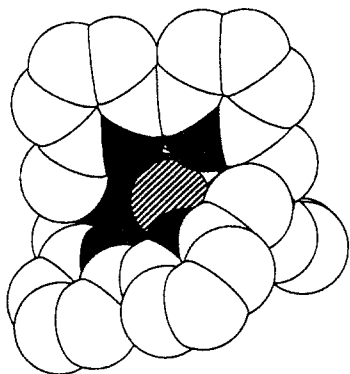


Fig. 2. Space-filling model of the compound [Na(1)]. Open circles, carbon; shaded, nitrogen; striped, sodium.

The compound could contain a neutral sodium *atom* within the cage, or it could contain a positive sodium *ion* with the 'missing' electron residing elsewhere. A sodium ion is much smaller than a sodium atom, and the crystal structure clearly indicates that it is an ion which is present (indeed the structure is very similar to a related cryptand complex [Na(crypt)]Br which unambiguously contains Na^+) [3]. Is the blue material an isolated $[\text{Na}(\mathbf{1})]^+$ cation, or is the elusive electron present?

One possibility is that the anion required for electrical neutrality is simply an electron. Such 'electride' salts are now well-established [4], and are associated with encapsulating ligands such as **1**. However, in these electride salts the electron is located in relatively large 'empty' sites within the crystal lattice where one might expect an anion. Unfortunately, no such vacancies are found within the lattice of the blue compound, in which the $[\text{Na}(\mathbf{1})]$ units are tightly packed. Where else could the electron be?

Lehn and colleagues propose that their compound represents a compromise between the charge-separated structure of an electride, $[\text{Na}(\mathbf{1})]^+e^-$, and that of an encapsulated metal atom, $[\text{Na}^0(\mathbf{1})]$. They suggest that the unique properties of the 2,2'-bipyridine units in ligand **1** allow the electron to reside on the pyridine rings of the cage. In other words, the structure may be represented as $[\text{Na}^+(\mathbf{1}^-)]$, in which $(\mathbf{1}^-)$ represents the radical anion of the ligand. Evidence of this comes from the displacement of the sodium from the centre of the cage towards one of the three 2,2'-bipyridine units ($\text{Na}-\text{N}_{\text{short}} \approx 2.6 \text{ \AA}$; $\text{Na}-\text{N}_{\text{long}} > 2.8 \text{ \AA}$). One of the properties of 2,2'-bipyridine which makes it of such value to the transition-metal coordination chemist is the presence of low-lying unoccupied π^* orbitals which provide a 'sink' for any excess electron density on metal centres [5]. It is suggested that the 2,2'-bipyridine residue that the sodium is closest to has accepted that missing electron, and now possesses the character of the bipy^- radical anion. The authors propose the use of the generic term 'cryptatium' for these compounds, with $[\text{Na}^+(\mathbf{1}^-)]$ being sodio-cryptatium.

This now offers the intriguing possibility for the synthetic chemist to fill the continuum of structural types between a neutral metal atom and the spatially separated electrides. If the cage ligand does not contain a 2,2'-bipyridine, then the charge-separated species are obtained. For example, the reaction of the cryptand **2**

(Figure 1) with one equivalent of potassium metal gives shiny black crystals of the electride salt, $[K(2)]^+e^-$ which behaves like a molecular metal [6]. However, the situation is not quite so simple, and even in these cases there are other sites in which the electron may reside. Of these, one of the less likely is on another metal ion to give a metal anion, but this is exactly what happens when **2** is allowed to react with an excess of sodium to give beautiful gold-coloured crystals of the salt $[Na(2)]^+Na^-$, which contains a 'sodide' anion [7]. This structure challenged many of the then existing conceptions regarding the alkali metals.

The unusual properties conferred upon metal ions when they are trapped in a cage have been explored by many workers. For several years, Sargeson has made detailed studies of the properties of metal ions within cages such as **3** (Figure 1), and has demonstrated the remarkable stabilization of 'unusual' oxidation states upon encapsulation [8]. For example, the reduction of $[Co(3)]^{3+}$ to $[Co(3)]^{2+}$ is facile and gives a cation that is very long-lived in solution. This is in contrast to the properties of conventional cobalt (II) amine complexes, which are very labile and would be expected to dissociate. The stability is ascribed to the inability of the cobalt (II) ion to 'squeeze' between the bars of the cage in which it is imprisoned.

The ambiguities associated with the formalization of charge distributions are well-known to inorganic and bioinorganic chemists, and there are many molecules such as 2,2'-bipyridine whose behaviour may be described as non-innocent. Dioxxygen is a prime example of such a ligand, and there is still controversy over the electronic nature of the oxygenated form of haemoglobin [9]. Should the $Fe(O_2)$ pair be formulated $Fe^{II}(O_2)$, $Fe^{III}(O_2^-)$ or $Fe^{IV}(O_2^{2-})$? Complexes of 2,2'-bipyridine have traditionally presented problems, and many apparently low-valent compounds should be formulated [5] as ligand and radical complexes such as $[M^{III}(bipy^-)_3]$ rather than $[M^0(bipy)_3]$. The niceties of this ambiguity are of direct relevance, as the complex cation $[Ru(bipy)_3]^{2+}$ plays a vital role in many chemical photoconversion systems. The critical excited state $[Ru(bipy)_3]^{2+*}$ is best described [10] as charge-separated $[Ru^{III}(bipy)_2(bipy^-)]^{2+*}$.

The new compound described by Lehn and co-workers provides a structural model for this photoexcited state as well as challenging our preconceptions about the ionic state. These new compounds may be regarded as 'expanded' elements, in which the effective size of the alkali metal atom has been increased – instead of finding the electron in one of the valence orbitals of the metal ion it is found slightly out in the orbitals of the directly bonded ligands.

References

1. L. Echegoyen, A. DeCian, J. Fischer and J.-M. Lehn: *Angew. Chem. Int. Ed. Engl.* **30**, 838–840 (1991).
2. L. F. Lindoy: *The Chemistry of Macrocyclic Complexes*, Cambridge University Press, 1989.
3. A. Caron, J. Guilhem, C. Riche, C. Pascard, B. Alpha, J.-M. Lehn and J.-C. Rodriguez-Ubis: *Helv. Chim. Acta.* **68**, 1577–1582 (1985).
4. J. L. Dye and R.-H. Huang: *Chem. Brit.* **26**, 239–244 (1990).
5. E. C. Constable: *Adv. Inorg. Chem.* **34**, 1–63 (1989).
6. R.-H. Huang, M. K. Faber, K. J. Moeggenborg, D. L. Ward and J. L. Dye: *Nature* **331**, 599–601 (1988).
7. F. J. Tehan, B. L. Barnett and J. L. Dye: *J. Am. Chem. Soc.* **96**, 7203–7208 (1974).
8. A. M. Sargeson: *Chem. Brit.* **15**, 23–27 (1979).
9. M. N. Hughes: In *Comprehensive Coordination Chemistry*, Vol. 6, G. Wilkinson, R. D. Gillard and J. A. McCleverty (Eds.), Pergamon, Oxford, 1987, pp. 541–754.